

DERWENT-ACC- 1997-221895**NO:****DERWENT- 200330****WEEK:****COPYRIGHT 1999 DERWENT INFORMATION LTD****TITLE:** Conductive resin paste - containing silver@ powder, cyclo:siroxane, compound containing alkenyl groups, and platinum catalyst**PATENT-ASSIGNEE: SUMITOMO BAKELITE CO LTD[SUMB]****PRIORITY-DATA: 1995JP-0223224 (August 31, 1995)****PATENT-FAMILY:**

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INT-CL (IPC): C08K003/08, C08K005/10 , C08L083/04 , H01B001/22 , H01L021/52**ABSTRACTED-PUB-NO: JP 09067518A****BASIC-ABSTRACT:**

In a conductive resin paste having (A) silver powder, (B) a cyclosiloxane of formula (I), (C) a compound having at least two alkenyl groups in the molecule and having a boiling point of at least 100 deg. C, and (D) a platinum-containing catalyst as the essential component, 60-90 wt.% of component (A), 1-20 wt.% of component (B), 5-25 wt.% of component (C), and 0.1-100 ppm of component (D) reduced into platinum are contained, (where R1, R2,R3 = methyl, or phenyl; m = integer of at least 2; and n = integer, provided that the sum of m and n is 3-6.

USE - Used as a conductive resin paste to bond semiconductor elements such as IC or LSI to a metallic frame, a ceramic base or an organic base such as glass epoxy.

ADVANTAGE - The conductive resin paste can be cured in a time not exceeding 30 seconds at 150 deg. C.

CHOSEN- Dwg.0/0**DRAWING:****TITLE-TERMS: CONDUCTING RESIN PASTE CONTAIN SILVER@ POWDER CYCLO SILOXANE COMPOUND
CONTAIN ALKENYL GROUP PLATINUM CATALYST****DERWENT-CLASS: A26 A85 L03 U11 X12****CPI-CODES: A06-A00E2; A08-D05; A08-M09A; A09-A03; A11-C01C; A12-E07C; L03-A01A3; L03-H04E4; L04-C17D;**

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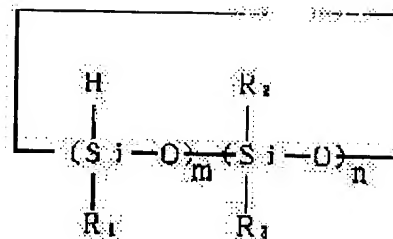
OKUBO HIKARI

(54) CONDUCTIVE PASTE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a conductive resin paste having a small amount of ionic impurities and improved in curability and workability by using a silver powder, a specified cyclosiloxane, a compound having a specified boiling point and containing an alkenyl group and a platinum catalyst as the essential components.

SOLUTION: This conductive resin paste is prepared by premixing 60-90wt.% silver powder containing 10ppm or below of ionic impurities (e.g. sodium ions) with 1-20wt.% cyclosiloxane represented by the formula (wherein R1 to R3 are CH3 or phenyl; (m) is 2 or greater; (n) is an integer; and m+n=3-6) and containing 500ppm or below ionic impurities (e.g. chloride ions and sodium ions), 5-25wt.% compound having two or more alkenyl groups in the molecule and having a boiling point of 100°C or above, 0.1-100ppm (in terms of the platinum atoms) of a platinum catalyst and optionally additives such as a flexibilizer, antifoamer and a coupling agent, kneading the obtained premix and deaerating the mixture in vacuo.



LEGAL STATUS

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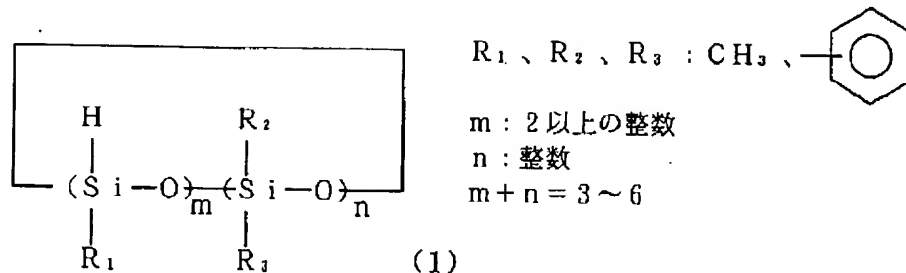
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CLAIMS

[Claim(s)]

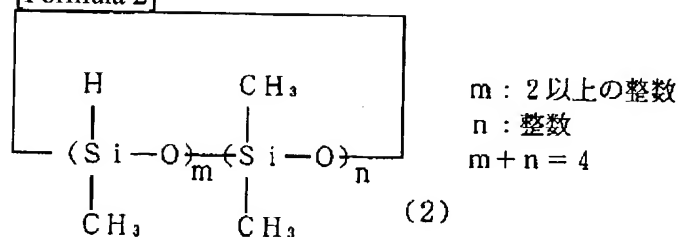
[Claim 1] The cyclosiloxane and (C) boiling point which are shown by silver dust and the (B) formula (1) (A) Above 100 degrees C And the compound and (D) platinum system catalyst which have two or more alkenyl radicals in 1 intramolecular are used as an indispensable component. And the conductive resin paste characterized by including the 1 - (C) component and including [the (A) component] 0.1-100 ppm of 5 - (D) components for the 60 - (B) component by platinum conversion 25% of the weight 20% of the weight 90% of the weight during [all] a conductive resin paste.

[Formula 1]



[Claim 2] The conductive resin paste according to claim 1 whose formula (1) is a formula (2).

[Formula 2]



[Claim 3] Claim 1 whose platinum system catalyst is the complex of platinum and cyclo (vinyl methyl siloxane), or a conductive resin paste according to claim 2.

[Claim 4] Claim 1 whose platinum system catalyst is the complex of platinum and divinyl tetramethyl disiloxane, or a conductive resin paste according to claim 2.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the conductive resin paste to which semiconductor devices, such as IC and LSI, are pasted up on a metal frame etc.

[0002]

[Description of the Prior Art] Adhesion of the semiconductor device in a semi-conductor production process and the in-line hardening method which arranged the die bonder, the wire bonder, etc. on the same Rhine for the purpose of improvement in productivity in the so-called die bond process are adopted, and it is in the inclination which will increase increasingly from now on. Therefore, as compared with the hardening conditions of the conductive resin paste by the batch method held from the former, the time amount which hardening takes was restricted remarkably, for example, in the case of the batch hardening method, it is 150-200 degrees C, and was hardening in 60 - 90 minutes, but in the case of the in-line hardening method, hardening for 15 - 90 seconds is demanded. Furthermore, a chip size is large, on the occasion of in-line hardening of the semi-conductor product which uses a copper frame, cold cure is required also for minimum-izing of the amount of curvatures of a chip and the chip based on the difference of the coefficient of thermal expansion of a frame, and antioxidizing of a frame, and hardening in a nearby short time is demanded about the setting time. Since high-boiling point solvents, such as a N-methyl-2-pyrrolidone and dimethylformamide, were used in the paste of a polyimide system used conventionally, hardening in a short time for 90 or less seconds was difficult, and since curing temperature had to be made into 250 degrees C or more making it harden for a short time, the void occurred remarkably during hardening and it had led to the fall of the properties of a semi-conductor product, such as a fall of adhesive strength, conductivity, and thermally conductive aggravation. On the other hand, although hardening in about 60 seconds is possible when using for example, an amine system curing agent etc. in the conductive paste of the epoxy system of the current mainstream, the correspondence to super-short-time hardening of 15 - 30 seconds is not made.

[0003]

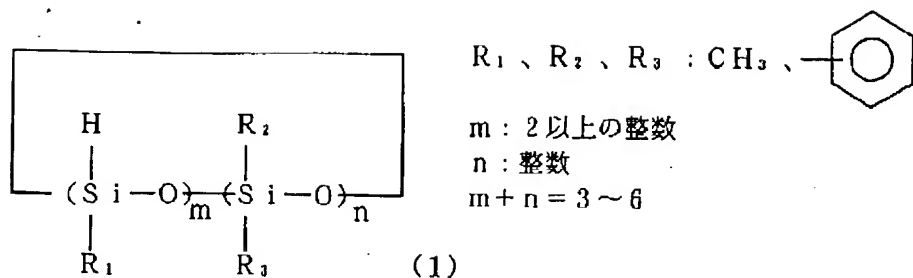
[Problem(s) to be Solved by the Invention] The conductive resin paste of high-reliability with few ionicity impurities, such as a chlorine ion and sodium ion, is offered that this invention can be hardened also on 150 degrees C or less and the hardening conditions for 30 or less seconds.

[0004]

[Means for Solving the Problem] The cyclosiloxane and (C) boiling point when this invention is shown by (A) silver dust and the (B) formula (1) are 100 degrees C or more. And the compound and (D) platinum system catalyst which have two or more alkenyl radicals in 1 intramolecular are used as an indispensable component. And it is the conductive resin paste which contains the 1 - (C) component 25% of the weight 20% of the weight, and contains [the (A) component] 0.1-100 ppm of 5 - (D) components for the 60 - (B) component by platinum conversion 90% of the weight during [all] a conductive resin paste.

[0005]

[Formula 3]

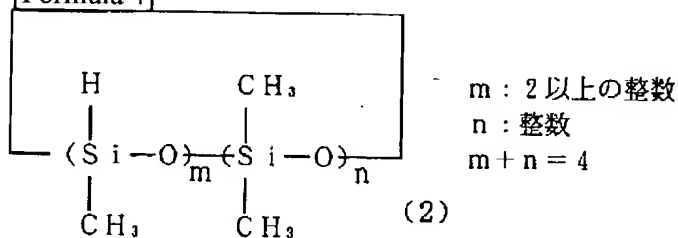


[0006] Since the fields to be used are an electron and an electric field, as for the silver dust used for this invention, it is desirable for the amounts of ionicity impurities, such as a chlorine ion and sodium ion, to be 10 ppm or less. moreover, independent [in the shape of a flake, arborescence, or a spherical thing] as a configuration -- or it can mix and use. Furthermore, about particle size, the about 50-micrometer thing of mean particle diameter is [2-10 micrometers and a maximum grain size] usually desirable, and it is desirable to mix comparatively fine silver dust and coarse silver dust, and to use. Since the electric conductivity of a hardened material will fall if the amount of silver dust under [all] conductive resin paste is less than 60 % of the weight, the viscosity of a resin paste will become high too much if 90 % of the weight is exceeded, and it becomes the cause of a fall of spreading workability, it is not desirable.

[0007] As for the cyclosiloxane of a formula (1) used by this invention, as for m, R1, R2, and R3 are two or more integers in a methyl group or a phenyl group, and m+n is 3-6. The thing of the structure shown by the formula (2) is more desirable, m is two or more integers, and m+n is 4.

[0008]

[Formula 4]



for example, in the 1, 1, 3, and 3-tetramethyl disiloxane which is a siloxane of the shape of a straight chain of different structure from the cyclosiloxane of a formula (1) The boiling point foams or volatilizes low with about 70 degrees C at the time of hardening, and when siloxane units are two or more so-called H oil Compatibility with the compound which has the alkenyl radical which serves as a partner of a reaction worsens, and these faults do not exist at the cyclosiloxane of a formula (1) to there being a fault separated at the time before hardening of hardening. As for the cyclosiloxane of a formula (1), it is desirable that ionicity impurities, such as chlorine and sodium, are 50 ppm or less. As these examples, tetramethyl cyclotetrasiloxane, hexa methyl cyclotetrasiloxane, pentamethyl cyclotetrasiloxane, etc. are mentioned. Since the engine performance which is 1 - 20 % of the weight, and is expected to be less than 1 % of the weight during [all] a conductive resin paste is not obtained, and sufficient structure of cross linkage will not be obtained if 20 % of the weight is exceeded, the loadings of the cyclosiloxane of a formula (1) cannot demonstrate adhesive strength with it. [the weak cohesive force of a conductive resin paste hardened material, and] [sufficient]

[0009] Although the boiling point is 100 degrees C or more, since it will foam or volatilize at the time of hardening if the boiling point is less than 100 degrees C, the compound which has two or more alkenyl radicals in 1 intramolecular used for this invention cannot be used. Moreover, the ANIKENIRU radical is required to consider a hydro silanizing reaction as cyclosiloxane, and in order that an alkenyl radical may not carry out macromolecule quantification even of after a reaction at 1 intramolecular at one case, it is not practical. In this invention, that the boiling point should just be 100 degrees C or more, the compound of the amount of macromolecules was expressed as 100 degrees C or more, in order to decompose before reaching at the boiling point. Since an alkenyl radical even with after [unreacted] hardening remains if the crosslinking density of the hardened material of a conductive resin paste will not become high, the engine performance needed for a conductive resin paste will not be obtained, if it is less than 5 % of the weight during [all] a conductive resin paste, and 25 % of the weight is exceeded, these loadings are not desirable. As a compound which has two or more alkenyl radicals in 1

intramolecular, it is 2-hydroxy. - It is 1, 3-JIMETAKURIROKISHI propane, 2, and 2-screw (4-(methacryloxydiethoxy) phenyl) propane, 1, 6-hexanedioldimethacrylate, 2, and 2-screw (4-(meta-chestnut ROKISHI ethoxy) phenol propane etc. is mentioned.).

[0010] Furthermore, although 6 chloroplatinic acid generally used at a hydro silanizing reaction as a platinum system catalyst may be used in this invention, there is little ion corrosive from the fields to be used being the electrical and electric equipment and the electronic field as much as possible, and it is desirable to use a complex with platinum, an organic compound, or an organic silicone compound from the point of catalytic activity. It is desirable to use the complex of platinum and cyclo (vinyl methyl siloxane) and the complex of platinum and divinyl tetramethyl disiloxane in that the complex itself reacts at the time of hardening although there are specifically platinum, a cyclo (vinyl methyl siloxane) complex and platinum, a divinyl tetramethyl disiloxane complex and platinum, an octyl alcohol complex, etc. During [all] a conductive resin paste, although it is 0.1-100 ppm in platinum conversion, if it is less than 0.1 ppm, a conductive resin paste will not fully harden, or, as for the loadings of a platinum system catalyst, the setting time becomes long. If 100 ppm is exceeded, the calorific value accompanying the reaction at the time of hardening of a conductive resin paste will increase too much, and a void causes [of the fall of bond strength, conductivity, and thermal conductivity] aggravation being easy to generate in a hardened material. In this invention, a flexible grant agent, a defoaming agent, a coupling agent, etc. can also be used if needed. After the manufacture approach of a conductive resin paste carries out preliminary mixing for example, of each component, bottom degassing of an after [kneading] vacuum of it is kneaded and carried out using 3 rolls, and it has obtained the resin paste.

[0011] This invention is concretely explained using an example below. The weight section shows the blending ratio of coal.

With one to example 4 particle size of 1-30 micrometers, flake-like silver dust with a mean particle diameter of 3 micrometers, Tetramethyl cyclotetrasiloxane (Toshiba Silicone and ** TSL 8249) (following silicone compound A), Hexa methyl cyclotetrasiloxane (Toshiba Silicone and ** TSL 8234) (following silicone compound B), 2-hydroxy - 1, 3-JIMETAKURIROKISHI propane (100 degrees C or more of boiling points) (following methacrylic compound A), the cyclo (vinyl methyl siloxane) solution (1 % of the weight of platinum concentration) (following platinum catalyst A) of the complex of platinum and cyclo (vinyl methyl siloxane), and a coupling agent (it ** Shin-Etsu Chemical Co., Ltd. -) It blended at a rate which shows KBM-503 in Table 1, it kneaded with 3 rolls, and the conductive resin paste was obtained. After carrying out the indirect desulfurization bubble of this conductive resin paste by 2mmHg by the vacuum chamber for 30 minutes, the following approaches estimated various engine performance.

[0012] Gel time: Paste 1cc was placed on the 150-degree C hot platen, and time amount until it stirs by the spatula and a paste stops showing a fluidity was measured.

** Whenever: The value in 25 degrees C and 2.5rpm was measured using E mold viscometer (3-degree cone), and it considered as viscosity.

Cobwebbing nature : The pin with a diameter [phi] of 1mm was put in to a depth of 5mm into the conductive resin paste, the pin was pulled up the rate for 300mm/, and height when a paste goes out was measured.

Volume resistivity: The paste was applied to 30 micrometers in width of face of 4mm, and thickness on slide glass, and the volume resistivity of the postcure object hardened for 30 seconds on 150-degree-C hot platen was measured.

Bond strength : using the paste, the 5x5mm silicon chip was mounted on the copper frame, and was hardened for 30 seconds on 150-degree-C hot platen. Die share reinforcement was measured using the push pull gage after hardening at the time of 240-degree C heat.

Void : observation of a void was performed for the sample before bond strength measurement with the soft-X-ray transmission method.

Impurity : the sodium and chlorine ion concentration of an extract which extracted 125 degree C of paste 2g and 40ml of pure water hardened and ground for 20 hours, and were obtained were measured with ion chromatography.

[0013] As a compound which has the alkenyl radical used example 5, 2 and 2-screw (4-(methacryloxydiethoxy) phenyl) propane (100 degrees C or more of boiling points) (following methacrylic compound B) was used together, and also the conductive resin paste was produced completely like examples 1-4, and it evaluated. As a platinum system catalyst used example 6, the xylene solution (3 % of the weight of platinum concentration) (following platinum catalyst B) of platinum and a divinyl tetramethyl disiloxane complex was used, and also the conductive resin paste was produced completely like examples 1-4, and it evaluated.

The conductive resin paste was produced completely like the example by the blending ratio of coal shown in one to example of comparison 6 table 2. In addition, in the example 5 of a comparison, instead of cyclosiloxane, it used 3-tetramethyl disiloxane (following silicone compound C), and methoxy diethylene-glycol methacrylate (100 degrees C or more of boiling points) (following methacrylic compound C) was used as 1, 1, 3, and a compound that has an alkenyl radical in the example 6 of a comparison. Since the examples 1-3 of a comparison were not hardened, they were impossible for evaluation of a property. An evaluation result is shown in Table 2.

[0014]

[Table 1]

表1

	実施例					
	1	2	3	4	5	6
銀粉	70.00	70.00	62.00	88.00	70.00	70.00
シリコン化合物A	9.98	6.09	12.73	3.78	5.25	9.98
シリコン化合物B		6.09				
メタクリル化合物A	18.99	16.79	24.23	7.20		19.01
メタクリル化合物B					23.72	
白金触媒A	0.03	0.03	0.04	0.01	0.03	
(白金換算値ppm)	3	3	4	1	3	
白金触媒B						0.01
(白金換算値ppm)						1.00
KBM503	1.00					
ゲルタイム (秒)	12	15	14	12	13	12
粘度 (PS)	80	84	60	114	136	76
糸引き性 (mm)	1	1	1	1	2	1
体積抵抗率 ($\times 10^{-4}\Omega \cdot \text{cm}$)	5	6	9	1	4	5
接着強度 (gf)	2000	1800	1850	2100	2050	1950
ボイド (%)	<5	<5	<5	<5	<5	<5
不純物	Na (ppm)	1	2	1	2	2
	Cl (ppm)	8	6	6	7	5
総合評価	○	○	○	○	○	○

[0015]

[Table 2]

表2

	比較例					
	1	2	3	4	5	6
銀粉	70.00	70.00	70.00	70.00	70.00	70.00
シリコン化合物A		28.97	9.99	9.37		
シリコン化合物C					10.71	
メタクリル化合物A	28.97		19.01	17.84	18.26	
メタクリル化合物C						21.98
白金触媒A	0.03	0.03		1.78	0.03	0.03
(白金換算値ppm)	3	3		178	3	3
KBM503	1.00					
ゲルタイム (秒)	>600	>600	>600	10	15	320
粘度 (PS)	92	62	136	82	78	74
糸引き性 (mm)	1	1	2	1	1	1
体積抵抗率 ($\times 10^{-4}\Omega \cdot \text{cm}$)				4	8	>10
接着強度 (gf)				1800	800	100
ボイド (%)				10~20	5~10	<5
不純物	Na (ppm)			1	1	2
	Cl (ppm)			6	7	8
総合評価	×	×	×	×	×	×

[0016]

[Effect of the Invention] The conductive resin paste of this invention is excellent in hardenability, and 150 degrees C and hardening in 30 or less seconds are possible for it. Moreover, the workability at the time of dispensing spreading is good, there are few ionicity impurities, and it can use for adhesion of semiconductor devices, such as IC to organic substrates, such as metal frames, such as 42 alloys, a ceramic substrate, and glass epoxy, and LSI.

[Translation done.]